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CORRELATION BETWEEN CHANGES IN LINEAR DIMENSIONS AND VOLUMETRIC PHASE COMPOSITION OF CERAMICS IN SINTERING

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The results of a dilatometric study of sintering for ceramics based on perlite rock and window glass under isothermic conditions are discussed. It is demonstrated that a modification of the geometrical dimensions of ceramics in sintering has a close functional relation to the modification of its volumetric phase composition. It is advisable to use the parameters characterizing this modification for kinetics studies, analysis, and mathematical description of the process of consolidation of ceramics in sintering.

Firing of materials gives rise to the physicochemical process of sintering, which is the process of thermal consolidation of a two-phase or, in the case of melt formation, a three-phase disperse system accompanied by increasing mechanical strength of the system and a modification of the volumetric ratio between the contents (parts) of the solid phase and the pores. A change in the volumetric phase composition of a sintered product is a consequence not only of changing apparent density ρ_{ap} due to aggregation of particles, but also the change in the true density ρ_t of the material during modification transformations, chemical (reaction), or physicochemical processes, which produce new phases or compounds. These changes directly influence the relative density $(K_s = \rho_{ap}/\rho_t)$ characterizing the volumetric part of the solid phase in the sintered article and also the values of the free pore space $(P = 1 - K_s)$, or the volumetric part of the pores. A comparison of the ratio between the volumetric parts of the solid phase and the pores in the initial (index 1), current, or final (index 2) state makes it possible to identify the direction and intensity of the sintering processes using the parameter n found from the formula

$$n = \frac{K_{s2}}{1 - K_{s2}} \frac{1 - K_{s1}}{K_{s1}}.$$

Different vectors of changes in the apparent and true density of materials in sintering determine the modifications of the geometrical size and volume of the product according to three main variants:

sintering is accompanied by a decrease in the linear size and volume of the body, which is possible under $\rho_{ap1} < \rho_{ap2}$, $\rho_{t1} \leq \rho_{t2}$, $K_{s2} > K_{s1}$, and $n > 1$;

the linear size and volume of the body remains constant in sintering, which is possible under $\rho_{ap1} = \rho_{ap2}$, $\rho_{t1} > \rho_{t2}$, $K_{s2} > K_{s1}$, and $n > 1$;

sintering is accompanied by an increase in the linear size and volume of the body, which is possible under $\rho_{ap1} \geq \rho_{ap2}$, $\rho_{t1} \geq \rho_{t2}$, or $\rho_{t1} < \rho_{t2}$, $K_{s2} < K_{s1}$, and $n < 1$.

In noncontact measurements of apparent and true porosity the determination of the parameter n does not cause special difficulties. However, not all researchers possess the necessary equipment; therefore, the purpose of the present study is to establish the possibility of using the results of dilatometric studies for identifying modifications in the volumetric phase compositions of articles that sinter according to variant 1, i.e., when the apparent density of articles increases due to their shrinkage while the true density of the material remains constant or slight ($\rho_{t1} \approx \rho_{t2}$).

Experimental samples of diameter 1.0 and length 2.5 cm were made by compression at a molding pressure of 20 MPa from two model batches with a specific surface area of 450 m^2/kg preliminarily calcined at a temperature of 500°C. Batch 1 consisted of perlite rock (60%) and window glass (40%) and had a true density of 2.59 g/cm^3, batch 2 with a true density of 2.61 g/cm^3 contained 70% perlite and 30% glass.

The shrinkage kinetics of the initial samples with $\rho_{ap1} = 1.34$ g/cm^3 and $K_{s1} = 0.517$ made of batch 1 was analyzed under isothermic conditions in a temperature range of 650 – 850°C with a step of 50°C. The sintering of samples of batch 2 with $\rho_{ap1} = 1.37$ g/cm^3 and $K_{s1} = 0.598$ was carried out in a temperature interval of 750 – 900°C. The obtained shrinkage values Δl of the samples were used to calculate the values $\Delta l/l_1$ and l_2/l_1, which were used to find the volumetric shrinkage and the ratio V_2/V_1 according to the formula

$$\frac{V_2}{V_1} = \left(\frac{l_2}{l_1}\right)^3,$$

where l_1, l_2, V_1, and V_2 are the length and the volume of the samples before and after sintering for a certain time, respectively.

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TABLE 1

τ, min	Δl, cm	l_2, cm	l_2/l_1	V_2/V_1	$\Delta l/l_1$, %	K_{s2}	ρ_{ap2}, g/cm^3	n	α_n, %	N, %
				Batch 1 at temperature 750°C						
0.5	0.026	2.474	0.989	0.969	1.04	0.533	1.425	1.068	6.36	3.31
1	0.045	2.455	0.982	0.947	1.79	0.545	1.555	1.123	10.95	5.79
2	0.097	2.403	0.961	0.888	3.87	0.582	1.650	1.302	23.19	13.45
3	0.135	2.364	0.945	0.846	5.41	0.611	1.776	1.468	31.88	19.46
4	0.163	2.336	0.934	0.816	6.54	0.633	1.849	1.615	38.08	24.01
5	0.178	2.332	0.928	0.801	7.12	0.645	1.891	1.700	41.17	26.50
6	0.186	2.314	0.925	0.793	7.43	0.652	1.913	1.750	42.85	27.95
8	0.200	2.299	0.919	0.778	8.02	0.664	1.954	1.850	45.94	30.43
10	0.216	2.283	0.913	0.762	8.65	0.678	1.999	1.971	49.26	33.33
12	0.228	2.271	0.908	0.750	9.13	0.689	2.032	2.073	51.76	35.61
				Batch 2 at temperature 850°C						
0.5	0.016	2.484	0.994	0.981	0.64	0.538	1.428	1.041	3.94	2.12
1	0.044	2.456	0.982	0.948	1.76	0.557	1.523	1.124	11.03	6.14
2	0.137	2.363	0.945	0.844	5.48	0.625	1.828	1.490	32.88	20.55
3	0.203	2.297	0.918	0.775	8.12	0.681	2.030	1.908	47.59	32.41
4	0.235	2.265	0.906	0.744	9.40	0.710	2.120	2.180	54.12	38.47
5	0.253	2.247	0.899	0.726	10.12	0.727	2.173	2.380	57.98	42.16
6	0.265	2.235	0.894	0.714	10.60	0.739	2.208	2.530	60.47	44.70
8	0.283	2.217	0.897	0.697	11.32	0.757	2.257	2.780	64.02	48.51
10	0.297	2.203	0.881	0.684	11.88	0.772	2.297	3.026	66.95	51.69
12	0.309	2.191	0.876	0.673	12.36	0.784	2.327	3.240	69.13	54.23

Data processing established that the ratios of sample volumes and their relative densities are related by the following dependence:

$$\frac{V_2}{V_1} = \frac{K_{s1}}{K_{s2}},$$

which can be used to calculate the value K_{s2} for any sintering duration, the parameter n, the degree of structure modification $\alpha_n = (n - 1)/n$, and the degree of filling or reduction of the initial pore volume (% or relative units) N according to the formula

$$N = \frac{K_{s2} - K_{s1}}{1 - K_{s1}}.$$

By way of example, Table 1 gives estimated and experimental data for sintering of samples of batches 1 and 2. For better presentation the values $\Delta l/l_1$, N, and α_n are given in percent. The analysis of these data indicates that the estimating parameters of the sintering process, n, α_n, and N, found from the modifications in the volumetric phase composition of ceramics, are more sensitive to changes occurring in the samples than the values $\Delta l/l_1$, l_2/l_1, V_2/V_1, and K_{s2}. It should be noted that the values K_{s2} characterize the degree of reaching the absolutely dense state, the values α_n — the degree of structure modification as a result of the decrease in the initial pore volume, and the value N shows the degree of filling of the initial pore space by the solid phase.

The parameter n characterizes the relative change in the absolute pore volume in sintering. All parameters proposed to estimate the process of material consolidation in sintering are closely interrelated and based on the values K_{s1} and K_{s2}:

$$K_{s2} = N(1 - K_{s1}) + K_{s1};$$

$$K_{s2} = \frac{K_{s1}}{(1 - \alpha_n) + \alpha_n K_{s1}};$$

$$K_{s2} = \frac{n K_{s1}}{(1 - K_{s1}) + n K_{s1}};$$

$$K_{s2} = \frac{N}{\alpha_n}.$$

Using the values of n and α_n it is possible to determine the apparent density of samples in sintering according to the formulas

$$\rho_{ap2} = \rho_{ap1}\left(2 - \frac{1}{n}\right)$$

or

$$\rho_{ap2} = \rho_{ap1}(1 + \alpha_n).$$

For a mathematical description of the consolidation of material it is important to select correctly not only the kinetic dependences but also the dependent variable characterizing the degree of transformation of the material in sintering. These variables, i.e., estimating parameters, reflect the modifications in the composition, structure, and properties of the material based on different physicochemical processes evolving in different ways with time.

If the ratio between different estimating parameters used to control the consolidation process is proportional and con-

TABLE 2

Batch	Ratio	Sintering duration, min									
		0.5	1	2	3	4	5	6	8	10	12
1	$\dfrac{\alpha_n}{\Delta l / l_1}$	6.11	6.11	5.99	5.89	5.82	5.78	5.76	5.73	5.69	5.67
	$\dfrac{N}{\Delta l / l_1}$	3.18	3.23	3.47	3.59	3.67	3.72	3.76	3.79	3.85	3.90
2	$\dfrac{\alpha_n}{\Delta l / l_1}$	6.15	6.26	6.00	5.86	5.75	5.73	5.70	5.65	5.63	5.59
	$\dfrac{N}{\Delta l / l_1}$	3.31	3.50	3.75	3.99	4.09	4.16	4.22	4.28	4.35	4.38

stant in time, which means that these variables respond similarly to the changes occurring in the material based on the same consolidation mechanism.

A deviation from this condition points to a different response of the estimating parameters to the modification of the material structure. For instance, a correlation of relative shrinkage values $\Delta l / l_1$ with the values α_n and N from Table 1 yields the results listed in Table 2.

A small variation (7 – 9%) of the ratio $\dfrac{\alpha_n}{\Delta l / l_1}$ in time can be attributed to the nearly identical response of the parameters $\Delta l / l_1$ and α_n to the material consolidation process. A substantial variation (up to 18 – 24%) of the ratio $\dfrac{N}{\Delta l / l_1}$ in time is due to the different physical meaning of these parameters; therefore, their use in kinetic dependences can result in a different degree of correlation between the estimated and experimental data.

The processing of data on isothermic sintering using the parameter n identified a linear dependence $n = f(\ln \tau)$ at different temperatures (Table 3).

By expressing the parameter n via its values α_n normalized within the interval of $0 – 1$, the kinetic equations $n = 1 + C \ln \tau$ can be represented in the following form:

$$\frac{\alpha_n}{1 - \alpha_n} = C \ln \tau,$$

where C is the constant of the material consolidation rate, min^{-1}.

The calculation of the apparent activation energy of the consolidation process based on the data from Table 3 indicates that the consolidation of samples of batch 1 is characterized by two activation energy values: $E = 177.7$ kJ/mole in the temperature interval of $650 – 750°C$ and $E = 43.5$ kJ/mole in the temperature interval of $750 – 850°C$. The consolidation of samples made of batch 2 is characterized by the single value $E = 156.7$ kJ/mole.

Some sintering specifics of the batches considered can be identified using kinetic dependences $n = f(\tau)$, which for all sintering temperatures can be represented by two rectilinear

TABLE 3

Sintering temperature, °C	Batch 1	Batch 2
650	$n = 1 + 0.067\ln \tau$	–
700	$n = 1 + 0.177\ln \tau$	–
750	$n = 1 + 0.437\ln \tau$	$n = 1 + 0.165\ln \tau$
800	$n = 1 + 0.548\ln \tau$	$n = 1 + 0.422\ln \tau$
850	$n = 1 + 0.688\ln \tau$	$n = 1 + 0.852\ln \tau$
900	–	$n = 1 + 1.648\ln \tau$

TABLE 4

Sintering temperature, °C	First stage ($\tau = 0 – 4$ min)	Second stage ($\tau > 4$ min)
650	$n = 1 + 0.03\tau$	$n = 1.06 + 0.0065\tau$
700	$n = 1 + 0.09\tau$	$n = 1.18 + 0.0203\tau$
750	$n = 1 + 0.15\tau$	$n = 1.42 + 0.0535\tau$
800	$n = 1 + 0.20\tau$	$n = 1.33 + 0.0915\tau$
850	$n = 1 + 0.27\tau$	$n = 1.31 + 0.1235\tau$

segments with different angles to the time axis and described by the equations specified in Table 4.

For the first stage of sintering the kinetic equation in a general form can be represented as $n = 1 + C\tau$ or, expressing the parameter n via its values α_n normalized in the interval of $0 – 1$, we obtain

$$C\tau = \frac{\alpha_n}{1 - \alpha_n}.$$

For the second stage of sintering the kinetic equation can be represented in the form of $n = n_0 + C_1 \tau$ or

$$C_1 \tau = \frac{1}{1 - \alpha_n} - n_0,$$

where C_1 is the constant of the structure modification rate, min^{-1}; n_0 is the required level of structure modification under an external energy impact to initiate the consolidation process at the second stage of sintering.

TABLE 5

Sintering temperature, °C	First stage ($\tau = 0 - 5$ min)	Second stage ($\tau > 5$ min)
750	$n = 1 + 0.050\tau$	$n = 1.15 + 0.025\tau$
800	$n = 1 + 0.116\tau$	$n = 1.29 + 0.077\tau$
850	$n = 1 + 0.290\tau$	$n = 1.85 + 0.116\tau$
900	$n = 1 + 0.606\tau$	$n = 2.65 + 0.320\tau$

Such evolution of the sintering process points to different mechanisms of ceramics consolidation at the early and later sintering stages; as the material reaches a state characterized by $n = 2.5$ and $K_{s2} > 0.7$, its consolidation rate significantly decreases, which points to another shift of the sintering mechanism, where diffusion processes become prevalent.

The process of consolidation of ceramics largely depends on its composition, primarily on a substantial content of glass. In the first stage thermal energy is spent on the final heating of the material to the sintering temperature and the glass particles reaching a premelting state. In this case the consolidation of the material occurs through the rearrangement of the solid phase particles due to the changing shape and decreasing volume of glass particles. At the second stage of sintering the compaction of the material occurs through the aggregation of the fused glass particles coming together under the effect of surface tension forces, the continuing melting of the glass particles, and physicochemical reactions of the viscous melt with the perlite rock particles, which have a higher melting temperature.

The parameters n and α_n are functionally interrelated and have the same physical meaning, therefore, the process rate constants found from kinetic dependences are equal as well. For instance, for batch 1 (Table 1) at $t = 750$°C and $\tau = 4$ min, the constant of the rate of the relative decrease of the absolute pore volume calculated based on the parameter n and the constant of the structure modification rate calculated based on α_n have the value $C = 0.153$ min^{-1}.

The constant of the rate of decrease of the initial pore volume calculated based on the equation $C\tau = \alpha_n /(1 - \alpha_n)$ substituting N instead of α_n has the value $C = 0.079$ min^{-1}, which shows a lower sensitivity of the estimating parameter N to the sintering processes.

The calculation of the apparent activation energy of ceramics consolidation according to the data of Table 4 indicates that both stages of the process are characterized by two activation energy values:

the first stage: $t = 650 - 750$°C, $E = 163.1$ kJ/mole; $t = 750 - 850$°C, $E = 57.0$ kJ/mole;

the second stage : $t = 650 - 750$°C, $E = 165.3$ kJ/mole; $t = 750 - 850$°C; $E = 79.9$ kJ/mole.

The high content of glass in batch 1 determines its substantial consumption of thermal energy on melting in the temperature interval of $650 - 750$°C, whereas the consolidation of ceramics mainly occurs due to the rearrangement of particles and this process has a rather high value of activation

energy ($E = 163 - 165$ kJ/mole). Under a more powerful impact on the material ($750 - 850$°C) the heat consumption on glass melting remains the same, but owing to a greater intensity of the heat flux the melting duration becomes significantly shorter and the melt viscosity sharply decreases, which has a favorable effect on its adhesion capacities. The consolidation of the material in this case occurs not only due to the continuing regrouping of particles, but also under the effect of contracting capillary (Laplace) forces, and the consolidation caused by the latter forces is prevailing and limiting. The involvement of free surface energy of the disperse material in the consolidation process by more than half decreases the need for external energy consumption, which is confirmed by the consolidation activation energy ($E = 57 - 80$ kJ/mole), due to viscous flow.

The evolution of consolidation in the sintering of samples made of batch 2 is similar to the consolidation of samples made of batch 1, but has some peculiarities (Table 5).

The consolidation of samples proceeds in two stages as well, and more intense consolidation occurs in the first stage due to the rearrangement of the initial glass particles caused by their surface fusion and shape modification. At this stage an external energy impact allows for reaching a certain level of the material structure modification and change of its physicochemical properties that is sufficient for subsequent less intense consolidation at the second stage due to the viscous flow determined by the surface tension force. The dependence $\ln C = f(1/t)$, in contrast to the dependence for batch 1, does not have a bend and each stage is characterized by a single value of the apparent activation energy of the consolidation process. For the first stage $E = 166$ kJ/mole, for the second stage $E = 169$ kJ/mole. The virtually equal energy levels of the process of material consolidation at the first and the second stages can be attributed to a higher relative density of the initial samples, a lower content of glass in the batch, and a wider sintering temperature interval. Consequently, it can be stated that the prevailing mechanism of consolidation in ceramics made of batch 2 is the rearrangement of particles, which requires higher energy consumption but at the same time ensures more intense compaction; moreover, the particle rearrangement process is facilitated by the surface tension force.

Thus, a modification of the geometrical sizes of ceramics in sintering has a clear functional correlation with the modification of its volumetric phase composition. It is advisable to use the parameters characterizing these changes in kinetic studies, analysis, and mathematical description of sintering evolving according to the first variant. Furthermore, the parameters n, α_n, and N can be rather effectively used to control the sintering process evolving according to the second variant, i.e., when the geometrical sizes of sintered products do not change and their consolidation occurs due to the increasing volume content of the solid phase determined by the decreasing true density of the material.